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(56) Documents cited
GB 1529493
GB 1517398
GB 1500559
GB 1436224
GB 1430634
US 4169121A
US 4144079A
US 4104214A
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(54) **Absorbent regenerated cellulose fibres**

(57) Regenerated cellulose fibres comprising anionically modified polysaccharides or their salts and having a crimping of at least 7%, may be prepared by adding an anionically modified polysaccharide to viscose and spinning the mixture at a collochemical ripening of 5 to 30° Hottenroth into a sulphuric acid spin bath, whereupon the resulting fibre bundle is drawn in a sulphuric acid secondary bath of a lower concentration. The mixed fibres, which exhibit a higher water and liquid retention capacity, are utilisable for tampons in women's hygienics, in the dental and surgical technologies, for sanitary towels, babies' napkins, sick-sheets, as well as for other disposable articles of general hygienics.

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SPECIFICATION

Improvements in or relating to a mixed fibre, its production, and utilisation

The invention relates to a mixed fibre exhibiting a high absorptive strength and a high liquid retention capacity on the basis of regenerated cellulose with a content of hydrophilic polymer additives, a method of producing them as well as their utilisation.

Absorptive materials, such as various cellulose materials, are known. In German patent No. 1,198,060 hydrophilic polyurethane foams are described. Also polymers, such as acryloamide, poly-N-vinylpyrrolidon (according to German Offenlegungsschrift No. 1,617,998) or wet-linked carboxymethylcellulose, which can be prepared for instance according to Swiss patent No. 491,140, have good absorptive properties. Viscous fibres containing one or more hydrophilic polymer substances, such as polyacrylic acid (German Offenlegungsschrift No. 23 24 589), poly-N-vinyl-pyrrolidon and if desired carboxymethylcellulose (German Offenlegungsschrift No. 25 50 345), alginic acid (German Offenlegungsschrift No. 27 50 622) or various copolymers (German Offenlegungsschrift No. 27 50 900), also have already been proposed. Such materials or fibres, in addition to exhibiting a high absorptive strength and a retention capacity for aqueous-physiological liquids that is high even under pressure influence, have to be excellently cardable and physiologically compatible. A prerequisite for a good compatibility is as low a content of extractable substances as possible.

Although the known absorptive materials partly exhibit a high water retention capacity according to DIN 53 814, they have only a moderate retention capacity for aqueous physiological liquids according to the Syngyna test, which means that absorptive bodies pressed of known absorptive materials are only to a limited extent capable of expanding against an external pressure when in contact with an aqueous-physiological liquid, of absorbing the same and of retaining the same against an external pressure.

The invention has as its object to improve these properties by providing high-crimped mixed fibres; it consists in that fibres of the initially defined kind contain, as a mixing component, anionically modified polysaccharides or their salts and have a crimping of at least 7%, measured as the change in length under a load of 1 cN/tex.

The term "crimping" denotes the relative change in length in per cent of a fibre under a load of 1 cN/tex.

A mixed fibre according to the invention suitably is comprised of 99 to 60%, preferably of 90 to 80%, regenerated cellulose and of 1 to 40%, preferably 10 to 20%, anionically modified polysaccharides.

According to a preferred embodiment, the fibre contains, as the mixing component, the ammonium or alkali-metal salt of, if desired slightly cross wet-linked, carboxymethylcellulose still soluble in a 6% aqueous soda lye, of carboxyethylcellulose, of carboxymethyl starch, of carboxyethyl starch, or of a mixture of these substances.

The invention also includes a method of producing these mixed fibres, which method is characterised in that

(a) at least one anionically modified polysaccharide, a salt thereof or an aqueous solution thereof, if desired with an alkali metal hydroxide admixed, is mixed with a viscose prepared of 25 to 40% mass, preferably 30 to 35 % mass, of carbon disulphide, based on the cellulose, and comprising a content of 4 to 9% mass of cellulose having an average degree of polymerisation of 400 to 600, furthermore a content of 0.2 to 0.3% mass of a modifier, such as a polyalkylene oxide, an alkoxylising product of ammonia, polyimines, fatty amines, fatty amides, or fatty alcohols.

(b) this mixture, when having a collochemical ripening of 5 to 30° Hottenroth (Ho), preferably 10 to 15° Ho, is spun at a temperature of 35 to 50°C, preferably 40°C, into a spin bath containing 50 to 80 g of sulphuric acid, preferably 60 to 65 g of sulphuric acid/l, 180 to 300 g of sodium sulphate/1, 30 to 50 g of zinc sulphate, preferably 40 g of zinc sulphate/1, the resulting fibre bundle preferably being guided over a deflection, and

(c) the fibre bundle is drawn by 70 to 120 %, preferably by 90 to 100 %, at 80 to 100°C, preferably at 90 to 95°C, in a secondary bath having a content of 2 to 30 g of sulphuric acid, preferably 5 to 10 g of sulphuric acid/1, of 5 to 80 g of sodium sulphate, preferably 20 to 40 g of sodium sulphate/1 and of 3 to 20 g of zinc sulphate, preferably 5 to 10 g of zinc sulphate/1, whereupon, if desired, the anionically modified polysaccharides contained in the fibres are converted into their alkali metal or ammonium salts.

A deflection of the fibre bundle in the spin bath additionally positively effects the absorption properties of the final fibres. After having passed the secondary bath, the mixed-fibre cable is cut and washed in a known manner, the mixing component being converted into a salt if desired, and then avived and dried.

Advantageously, the fibres according to the invention have a titer of 1.5 to 10.1, in particular of 1.5 to 5.5 dtex, and a length of 20 to 120 mm, in particular of 30 to 50 mm. It has furthermore proved

percentage of the incorporated anionically modified polysaccharide is to be as high as possible in the final fibre, based on the utilisation of the same in the production process of the fibres. By using a slightly cross wet-linked carboxymethylcellulose (CMC), the losses of the mixing component in the course of production can be reduced. The wet-linking may be performed with epichlorohydrin, the cross wet-linked CMC however has to be soluble in a 6 % aqueous soda lye.

The combination of the anionically modified polysaccharide incorporated in the fibres of the invention and of a high crimping degree is decisive for their high absorptive strength and in particular for their high liquid retention capacity. Accordingly, a main field of application of the fibres according to the invention having a water retention capacity (WRC) of at least 140%, but primarily a liquid retention capacity according to the Syngyna test of at least 7.0 g/g, is their processing into tampons for women's hygienics, for the dental and surgical technologies, into sanitary towels, babies' napkins, sick-sheets as well as other disposable articles of general hygienics.

The fibres according to the invention retain their excellent absorption properties even under pressure influence.

For investigating this specific characteristic feature, a modified Syngyna test was carried out. The expansion of a test tampon was determined 1 minute, 3 minutes, and 15 minutes after the addition of a blood-substitute solution against a membrane being under a pressure of 16.7 mbar by collecting the water amount displaced and weighing the same. The blood substitute solution used is composed of:

70 g of hydroxyethylcellulose having an average substitution degree of about 2 and a mean molar weight of about 40,000 (Tylose H 20 of Hoechst)

50 g of NaCl

20 g of $NaHCO_3$

500 g of glycerol

Addition of water to 5,000 ml.

The values for the liquid uptake after 15 minutes were determined by reweighing.

As the characteristic value, the figure resulting from the division of the totally absorbed liquid amount in g by the dry weight of the tampon in g (liquid retention capacity) is determined.

The determination of the water retention capacity (WRC) was carried out according to DIN 53 814.

The production of an absorptive body will be described in more detail in the following: the fibre material was carded and the card web obtained was pressed into cuboid-shaped test tampons of the dimension 50 x 20 x 6 mm, which, having a length of 50 mm, a weight of 2.8 g and a density of 0.5 g/cm^3, correspond approximately to a commonly available tampon.

For the comparison of the utilisation qualities of absorptive material produced of fibres according to the invention and those of absorptive materials produced of known fibres, a series of test absorptive bodies was produced of fibres.

In examples 1 to 4, fibres were produced according to the invention, in example 5 fibres were produced of regenerated cellulose without the addition of an anionically modified polysaccharide, and in example 6 fibres were produced on the basis of regenerated cellulose with an admixture of CMC, but with little crimping.

EXAMPLE 1

179 g of a solution containing 6 % carboxymethylcellulose and 6 % soda lye were mixed into 1 kg of viscose containing 6.1 % cellulose, 5.9 % soda lye, 1.5 % sulphur and 0.3 % of an alkylated aminoxethylate. The mixture thus prepared contained 5.7 % cellulose, 6.0 % soda lye, 1.4 % sulphur and 0.3% of an alkylated aminoxethylate and was spun into a spin bath containing 65 g of H_2SO_4, 230 g of Na_2SO_4 and 40 g of $ZnSO_4$, per liter at a ripening of 13.2° Hottenroth. The temperature of the spin bath was 40°C. The coagulated fibre cable was drawn by 100 % in a secondary bath containing 5 g of H_2SO_4, 30 g of Na_2SO_4 and 5 g of $ZnSO_4$, per litre, and having a temperature of 95°C. Subsequently, the continuous fibres were cut into staples, washed, bleached, avived and dried.

The fibres showed the following average properties:

Titer (dtex):	5.5
Staple length (mm):	40

WRC according to DIN 53 814 (%): 146

EXAMPLE 2

179 g of a solution containing 6 % carboxymethylcellulose and 6 % soda lye were mixed into 1 kg of viscose containing 6.0 % cellulose, 6.0 % soda lye, 1.7 % sulphur and 0.3 % of an alkylated aminoxethylate, and the mixture thus prepared, which contained 5.8 % cellulose, 6.0 % soda lye, 1.6 % sulphur and 0.3 % of an alkylated aminoxethylate, was spun at a ripening of 13.7° Hottenroth. The spin bath had a temperature of 40°C and contained 65 g of H_2SO_4, 230 g of Na_2SO_4 and 40 g of $ZnSO_4$ per litre. In a secondary bath, which contained 5 g of H_2SO_4, 30 g of Na_2SO_4 and 5 g of $ZnSO_4$ per liter and which had a temperature of 95°C, the fibre bundle was drawn by 108%. The further processing was performed as in Example 1.

The average properties of the fibres were as follows:

Titer (dtex): 5.5

Staple length (mm): 40

Crimping (%/cN/tex): 8.3

WRC according to DIN 53 814 (%): 139

EXAMPLE 3

179 g of a solution containing 6 % carboxymethylcellulose and 6 % soda lye were mixed into 1 kg of viscose containing 6.0 % cellulose, 5.9 % soda lye, 1.7 % sulphur and 0.3 % of an alkylated aminoxethylate. The mixture thus prepared contained 5.8 % cellulose, 6.1 % soda lye, 1.6 % sulphur and 0.3 % of an alkylated aminoxethylate and was spun at a ripening of 11.2° Hottenroth into a spin bath containing 65 g of H_2SO_4, 230 g of Na_2SO_4 and 40 g of $ZnSO_4$ per litre and having a temperature of 40°C. The fibre bundle was drawn by 102% in a secondary bath containing 5 g of H_2SO_4, 30 g of Na_2SO_4 and 5 g of $ZnSO_4$ per litre, and was further processed as in Example 1.

The fibres showed the following average fibre properties:

Titer (dtex): 5.5

Staple length (mm): 40

Crimping (%/cN/tex): 7.3

WRC according to DIN 53 814 (%): 148

EXAMPLE 4

220 g of a solution containing 6 % carboxymethyl starch and 6 % soda lye were mixed into 1 kg of viscose containing 5.9 % cellulose, 5.9 % soda lye, 1.8 % sulphur and 0.3 % of an alkylated aminoxethylate. The mixture thus prepared contained 5.9 % total polyglycoside, 5.8 % soda lye, 1.4 % sulphur and 0.3 % of an alkylated aminoxethylate and was spun at a ripening of 12.8° Hottenroth into a spin bath containing 65 g of H_2SO_4, 230 g of Na_2SO_4 and 40 g of $ZnSO_4$ per litre and having a temperature of 40°C. The fibre bundle was drawn by 95% in a secondary bath containing 5 g of H_2SO_4, 30 g of Na_2SO_4 and 5 g of $ZnSO_4$ per litre and having a temperature of 95°C, and was further processed as in Example 1.

The average properties of the fibres were as follows:

Titer (dtex): 5.5

Staple length (mm): 40

Crimping (%/cN/tex): 10.3

WRC according to DIN 53 814 (%): 150

(COMPARATIVE) EXAMPLE 5

A viscose was prepared containing 6.0 % cellulose, 6.2 % soda lye, 1.5 % sulphur and 0.3 % of an alkylated aminoxethylate. This viscose was spun into a spin bath containing 65 g of H_2SO_4, 230 g of Na_2SO_4 and 40 g of $ZnSO_4$ per litre at a ripening of 13.0° Hottenroth. The spin

cut into staples, washed, bleached, avived and dried.

The fibres showed the following average properties:

Titer (dtex):	5.5
Staple length (mm):	40
Crimping (%/cn/tex):	10.4
WRC according to DIN 53 814 (%):	86

(COMPARATIVE) EXAMPLE 6

179 g of a solution containing 6 % carboxymethylcellulose and 6 % soda lye were mixed into 1 kg of viscose containing 6.0 % cellulose, 5.7 % soda lye, 1.8 % sulphur and 0.2 % of an alkylated aminoxethylate. The mixture thus prepared contained 5.7 % cellulose, 5.6 % soda lye, 1.4 % sulphur and 0.2 % of an alkylated aminoxethylate and was spun at a ripening of 13.2° Hottenroth into a 40°C hot spin bath containing 73 g of H_2SO_4, 107 g of Na_2SO_4 and 62 g of $ZnSO_4$ per litre. The fibre bundle was drawn by 108 % in a secondary bath containing 20 g of H_2SO_4 per litre and having a temperature of 95°C, and was further processed as in (comparative) example 5.

The average properties of the fibres were as follows:

Titer (dtex):	5.5
Staple length (mm):	40
Crimping (%/cn/tex):	5.2
WRC according to DIN 53 814 (%):	148

The properties determined at the test absorptive bodies are summarised in the following table:

Suction body of fibres according to Example	Expansion in ml, after			Total amount absorbed of blood-substitute liquid after 15 minutes, in g	Liquid retention capacity according to Syngyna test (g/g)
	1 min	3 min	15 min		
1	6.6	10.8	16.7	22.2	7.93
2	6.0	11.3	16.3	21.5	7.68
3	4.1	9.6	14.9	19.8	7.07
4	6.5	12.6	14.9	20.0	7.14
5	5.4	10.7	12.6	17.0	6.07
6	4.2	9.0	11.8	18.5	6.61

The comparison shows that the values for the expansion after 15 minutes as well as the values for the liquid amount absorbed are increased with the materials comprised of the fibres according to the invention as compared to the absorptive bodies made of fibres according to (comparative) examples 5 and 6.

The method according to the invention will now be explained in even more detail by the following examples 7 and 8:

EXAMPLE 7

135 g of a solution containing 6 % carboxymethylcellulose with an average substitution degree of 0.97 and containing 6 % soda lye were mixed into 1 kg of viscose containing 6.1 % cellulose, 5.9 % soda lye, 1.8 % sulphur and 0.3 % of an alkylated aminoxethylate. The mixture thus prepared contained 5.8 % cellulose, 5.8 % soda lye, 1.7 % sulphur and 0.3 % of an alkylated aminoxethylate and was spun

secondary bath containing 5 g of H_2SO_4, 30 g of Na_2SO_4 and 5 g of $ZnSO_4$ per litre and having a temperature of 95°C, and was further processed as in Example 1.

On account of a content of the fibres of carboxyl groups amounting to 1.44 %, a yield in carboxymethylcellulose of 65 % is obtained.

EXAMPLE 8

Into 1 kg of a viscose having a composition as that of Example 7, 146 g of a solution were mixed which contained 6 % of a slightly wet-linked carboxymethylcellulose with an average substitution degree of 0.87 and 6 % soda lye. The mixture thus prepared contained 5.9 % cellulose, 6.0 % soda lye, 1.8 % sulphur and 0.3 % of an alkylated aminoxethylate and was spun at a ripening of 11.0° Hottenroth into a spin bath containing 65 g of H_2SO_4, 230 g of Na_2SO_4 and 40 g of $ZnSO_4$ per litre and having a temperature of 40°C. The fibre bundle was drawn by 108% in a secondary bath containing 5 g of H_2SO_4, 30 g of Na_2SO_4 and 5 g of $ZnSO_4$ per litre and having a temperature of 95°C, and was processed further as in Example 1.

On account of a content of the fibres of carboxyl groups amounting to 1.68 %, a yield in carboxymethylcellulose of 77 % was obtained.

CLAIMS

1. A mixed fibre exhibiting a high absorptive strength and a high liquid retention capacity on the basis of regenerated cellulose having a content of hydrophilic polymer additives, characterised in that the fibre contains, as a mixing component, anionically modified polysaccharides or their salts, and has a crimping of at least 7%, measured as the change in length under a load of 1 cN/tex.

2. A mixed fibre according to claim 1, characterised in that it comprises 99 to 60 %, preferably 90 to 80 % regenerated cellulose and 1 to 40 %, preferably 10 to 20 %, anionically modified polysaccharides or their salts.

3. A mixed fibre according to claim 2, characterised in that it comprises, as the mixing component, the ammonium or alkali-metal salt of, if desired slightly cross wet-linked, carboxymethylcellulose still soluble in a 6% aqueous soda lye, of carboxyethylcellulose, of carboxymethyl starch, of carboxyethyl starch or of a mixture of these substances.

4. A method of producing mixed fibres according to claims 1 to 3, characterised by

(a) mixing at least one anionically modified polysaccharide, a salt thereof or an aqueous solution thereof mixed if desired with an alkali metal hydroxide, with a viscose prepared of 25 to 40 % mass, preferably 30 to 35 % mass, of carbon disulphide, based on the cellulose, and having a content of 4 to 9 % mass of cellulose of an average polymerisation degree of 400 to 600, furthermore a content of 0.2 to 0.3 % mass of a modifier, such as a polyalkyleneoxide, an alkoxylation product of ammonia, polyimines, fatty amines, fatty amides or fatty alcohols,

(b) spinning the mixture at a collochemical ripening of 5 to 30° Hottenroth (Ho), preferably 10 to 15° Ho, at a temperature of 35 to 50°C, preferably 40°C, into a spin bath containing 50 to 80 g of sulphuric acid, preferably 60 to 65 g of sulphuric acid/1, 180 to 300 g of sodium sulphate/1, 30 to 50 g of zinc sulphate, preferably 40 g of zince sulphate/1, the resulting fibre bundle preferably being guided over a deflection, and

(c) drawing the fibre bundle by 70 to 120 %, preferably by 90 to 100 %, at a temperature of 80 to 100°C preferably 90 to 95°C, in a secondary bath having a content of 2 to 30 g of sulphuric acid, preferably 5 to 10 g of sulphuric acid/1, of 5 to 80 g of sodium sulphate, preferably 20 to 40 g of sodium sulphate/1 and of 3 to 20 g of zinc sulphate, preferably 5 to 10 g of zinc sulphate/1, whereupon the anionically modified polysaccharides contained in the fibres, if desired, are converted into their alkali metal or ammonium salts.

5. Utilisation of the mixed fibre according to claims 1 to 3, the mixed fibre having a water retention capacity of at least 140% and a liquid retention capacity according to the Syngyna test of at least 7.0 g/g, for tampons in women's hygienics, in the dental and surgical technologies, for sanitary towels, babies' napkins, sick-sheets as well as for other disposable articles of general hygienics.

6. A mixed fibre substantially as hereinbefore described with references to the accompanying examples.

7. A method of producing mixed fibres substantially as hereinbefore described with reference to the accompanying examples.

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